# *Cadmium Alternatives*

Mike Barnstead

ASETS Defense 2012

San Diego

# Report Documentation Page

*Form Approved*
*OMB No. 0704-0188*



| | | |
|---|---|---|
| 1. REPORT DATE<br>**AUG 2012** | 2. REPORT TYPE | 3. DATES COVERED<br>**00-00-2012 to 00-00-2012** |
| 4. TITLE AND SUBTITLE<br>**Cadmium Alternatives** | | 5a. CONTRACT NUMBER |
| | | 5b. GRANT NUMBER |
| | | 5c. PROGRAM ELEMENT NUMBER |
| 6. AUTHOR(S) | | 5d. PROJECT NUMBER |
| | | 5e. TASK NUMBER |
| | | 5f. WORK UNIT NUMBER |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)<br>**MacDermid,245 Freight Street,Waterbury,CT,06702** | | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | 10. SPONSOR/MONITOR’S ACRONYM(S) |
| | | 11. SPONSOR/MONITOR’S REPORT NUMBER(S) |

12. DISTRIBUTION/AVAILABILITY STATEMENT
**Approved for public release; distribution unlimited**

13. SUPPLEMENTARY NOTES
**ASETSDefense 2012: Sustainable Surface Engineering for Aerospace and Defense Workshop, August 27-30, 2012, San Diego, CA. Sponsored by SERDP/ESTCP.**

14. ABSTRACT

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT<br>**unclassified** | b. ABSTRACT<br>**unclassified** | c. THIS PAGE<br>**unclassified** | **Same as Report (SAR)** | **59** | |

# *Cadmium – The Need for Change*

- Cadmium passivated with hexavalent chromium has been in use for many decades
- Cadmium is toxic, and is classified as a priority pollutant, hazardous substance, hazardous air pollutant, & hazardous waste
- Safety and environmental regulations
  - RoHS, ELV, WEEE, REACH, et. al.
  - Executive Orders 13514 & 13423
  - DoD initiatives –
    - Young memo (April 2009)
    - DFAR restricting use of hexavalent chromium
      - Allows the use of hexavalent conversion coatings
- Performance requirements also driving change
  - Weight reduction, new performance criteria
  - Wider use of composites, 336 / 772 hours $SO_2$, etc

MacDermid

# *Some Specifications with Cd Alternatives*

- MIL-DTL-38999
- MIL-DTL-28840
- MIL-DTL-26482
- MIL-DTL-83723
- MIL-DTL-22992
- MIL-DTL-83513
- MIL-DTL-24308
- MIL-DTL-83733
- MIL-PRF-28876

## *Presentation Overview*

- The goal of this presentation is to review what we know about cadmium alternatives
- None of the commercially available cadmium alternatives are “drop-in” replacements
  - All of the available coatings have some issue, including cadmium!

MacDermid

## *Cadmium Replacements (With MIL-DTL-38999 Designations)*

- Zn/Ni (Class Z)
  - Per ASTM B 841, type D (black)
- Electroless Nickel plus PTFE (Class T)
  - New spec - AMS 2454
- Electroplated Al (Class P)
  - Per MIL-DTL-83488, Type II
- All must be able to pass 500 hrs NSS (1000 hrs for accessories) and be non-reflective

## *Cadmium Replacements – Zinc Nickel*

- Passivated Zinc Nickel
  - Non-hex chrome passivate of high interest, but hexavalent passivate most common due to conductivity issues and DFAR Cr+6 passivate exemption
- Major hurdles seen with Zn/Ni
  - Adhesion (chipping) – has been largely addressed with some LHE processes
  - Conductivity – Needs improvement
    - Both $Cr^{+6}$ and $Cr^{+3}$ passivates

MacDermid

## *Cadmium Replacements – Zinc Nickel*

- Alloy needs clarification
  - 38999 specifies Zn/Ni per ASTM B841 - Standard Specification for Electrodeposited Coatings of Zinc Nickel Alloy Deposits
    - Calls for 12% Ni maximum
  - Most industry call outs are for 12 to 15% Ni
    - 14% gives better corrosion resistance
- Zn/Ni is a sacrificial (anodic) coating when plated over steel, copper, or nickel

## *Cadmium Replacements - EN / PTFE*

- No major performance issues seen
  - Major hurdle was predicted galvanic problem with legacy coatings like cadmium
  - Testing shows galvanic behavior of EN/PTFE is different from nickel
- Major hurdles seen with EN/PTFE
  - Concerns about PTFE status as a PFC
  - Concerns about out-gassing in a fire
  - EN/PTFE is normally a barrier (cathodic) coating

## *Cadmium Replacements – Electrodeposited Aluminum*

- Electrodeposited Al coating has unique features, but coating not ideal for connectors
- Major hurdles seen with Electroplated Al
  - Production of conductive corrosion products (ASETS 2009)
  - Galling during durability testing (addressed with a lube)
  - Flammable, high VOC electrolyte
  - Single source
- Cold spray and vapor deposited Al generating interest in some applications, but limited for connectors

# Other Alternatives

- High interest in black EN
  - Able to meet corrosion, durability, and conductivity requirements
  - Not 38999 approved
  - Many companies using for commercial applications
- Other zinc alloys
  - Zinc cobalt, tin zinc, zinc iron

## *Passivation*

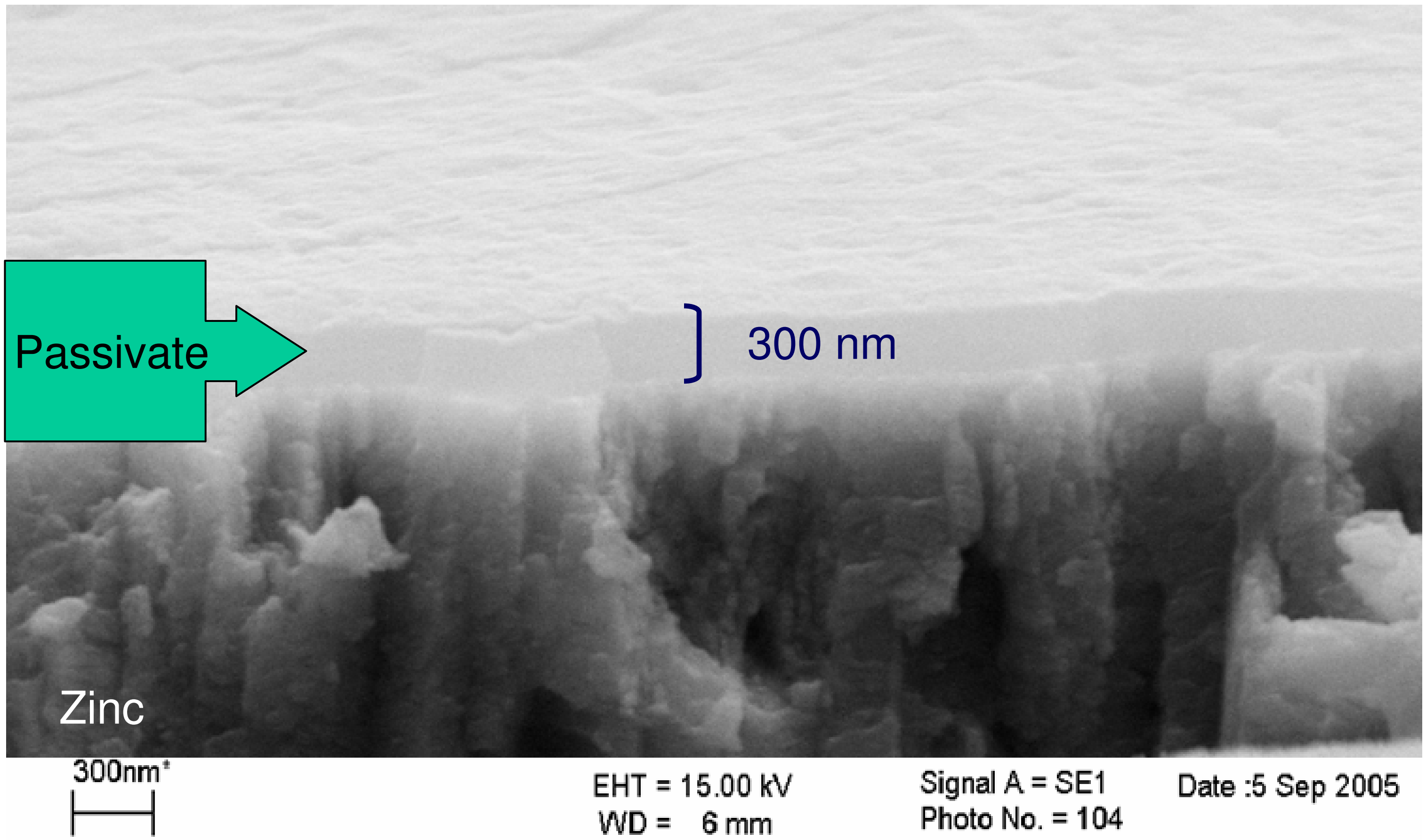
- Cadmium, ZnNi, SnZn, ZnCo, ZnFe, and electroplated aluminum are usually passivated to provide increased corrosion protection
  - Currently hexavalent chromates are primarily used
    - Toxic, carcinogenic, leachable
- Trivalent and non-chrome passivates generally struggle with conductivity

## *Major Differences in Trivalent vs. Hexavalent Passivates*

- Trivalent passivates build thicker films
  - Film thickness of trivalent passivates can be up to 4 times thicker than hexavalent passivates
  - This is why they have increased electrical resistance
- Trivalent passivates are not hydrated, so they have excellent thermal shock resistance
  - …but, are not self healing

# *Trivalent Passivate Film*

Cryo fractured SEM image of a **Trivalent Passivate**




MacDermid

# *Public Domain Test Results*

## *National Defense Center for Energy and Environment (NDCEE) 2010 Testing*

- Tested several cadmium alternatives
  - Electroplated zinc-nickel (ZnNi)
  - Electroless nickel / PTFE (Durmalon®)
  - Electroplated Aluminum (Alumiplate®)
  - Electroplated tin-zinc (SnZn)
  - Control: cadmium with hexavalent chromate
- Used non-hexavalent chromium passivates
  - Trivalent chromium (TCP)
  - Non-chromate post-treatment (NCP)

## *NDCEE Salt Spray Testing Results*

- Cadmium and electroless nickel / PTFE performed well
- Electroplated aluminum performed did not perform well on connectors
- Electroplated aluminum did not pass durability
- All SnZn and ZnNi failed

# *NDCEE Salt Spray Results*

CADMIUM CONNECTOR
ASTM B117
452 HRS MATED - 48 HRS UNMATED
RINSED AND CLEANED

DURMALON CONNECTOR
ASTM B117
452 HRS MATED - 48 HRS UNMATED
RINSED AND CLEANED

ALUMINPLATE TRI CR CONNECTOR
ASTM B117
452 HRS MATED - 48 HRS UNMATED
RINSED AND CLEANED

ELECTROPLATED ALKALINE ZINC
NICKEL TRI CR CONNECTOR
ASTM B117
452 HRS MATED - 48 HRS UNMATED
RINSED AND CLEANED

## *NDCEE – Conclusions*

- No candidate demonstrated performance as good as or better than cadmium in all tests
- SnZn (with both TCP and NCP) demonstrated unusually poor and inconsistent performance, failing nearly all tests
- ZnNi with TCP demonstrated unusually poor and inconsistent performance, particularly with respect to coating adhesion (chipping) and shell-to-shell conductivity

Full Presentation:
http://www.ndcee.ctc.com/documents/E2S2_2010/2139-10%20-%20Presentation.pdf

## *AIR5919 Rev. A*

- AIR5919 was updated in July 2010
- Provides test data on coatings from 7 sources
  - Ni/PTFE
  - ZnNi
  - Electrodeposited Aluminum
  - IVD aluminum
  - ZnCo
  - Cadmium control
- Ni/PTFE performed well in these tests, outperforming all other cadmium alternatives
- Oddly, cadmium performed poorly when mated to ZnNi or electrodeposited aluminum

# AIR5919 – TABLE 3 Single Shell Failures

| Coating | Source | Substrate | Failure(s) |
|---|---|---|---|
| IVD Al | Source 1 | PEEK | Conductivity |
| IVD Al | Source 1 | PEEK | NSS |
| IVD Al | Source 1 | PEEK | Post NSS conductivity |
| IVD Al | Source 1 | Aluminum | Durability |
| Electrodeposited Aluminum (Type 1) | Source 1 | PEEK | NSS |
| Electrodeposited Aluminum (Type 2) | Source 1 | PEEK | NSS |
| Electrodeposited Aluminum | Source 1 | Aluminum | NSS |
| Zinc Nickel | Source 2 | Aluminum | Post NSS conductivity |
| Zinc Cobalt | Source 2 | Aluminum | Post NSS conductivity |
| EN/PTFE (Teflon Ni) | Source 2 | SST | Post NSS conductivity |
| Zinc Nickel | Source 2 | SST | Post NSS conductivity |
| Zinc Cobalt | Source 2 | SST | Post NSS conductivity |
| Zinc Cobalt | Source 4 | Aluminum | NSS |

**NOTE – "Enslic" results omitted as only Source 2 provided results**

# MacDermid Testing Results

# *Cadmium Alternatives Testing*

- A large number of tests have been run and previously reported by MacDermid on a wide range of plated deposits
- Based on this testing and user feedback, we know
  1. When plating a sacrificial layer (cadmium, ZnNi, etc) medium phosphorus is usually acceptable
  2. When plating a barrier layer (electroless) high phosphorus is preferred
  3. The choice of aluminum alloy used can impact test results
  4. Pretreatment practices are critical and can dramatically skew results
  5. Machining operations can have a major impact on performance
  6. Part design can impact performance
  7. These results are generally accepted and will not be reported

## *Cadmium Alternatives Testing*

- Additional tests were run on the best performers from initial screening tests
  - EN/PTFE
  - Zinc Nickel
  - Black EN
- Tests applied
  - Adhesion
  - NSS
  - Conductivity (as plated and after 500 hrs NSS)
  - Electrochemical potential

# *Test Matrix*

- All parts were 6061 shells purchased on the open market
- All EN processes were RoHS compliant
- All samples received the same pretreatment process (non-nitric, non-fluoride)
- All parts had two plating layers
- Unless stated total thickness was between 25 to 30 um (1 to 1.2 mils)
- Top layer was one of the below:
  - 5 ums EN/PTFE (30% volume PTFE)
  - 8 ums Zn/Ni & hexavalent black passivation
  - 8 - 10 ums Black EN (electropassivated)

# 20 um High Phos / 5 um EN PTFE

96 hrs NSS

500 hrs NSS

1000 hrs NSS


MacDermid

# *EN PTFE NSS Conclusions*

- All EN PTFE parts passed 500 hrs NSS
  - Some salt retention on corners and edges
- After 1000 hrs all parts passed but showed increasing salt retention

# *20 um Mid Phos / 8 um Zinc Nickel*

96 hrs NSS

500 hrs NSS

1000 hrs NSS

# 20 um High Phos / 8 um Zinc Nickel

96 hrs NSS

500 hrs NSS

1000 hrs NSS

## *Zinc Nickel NSS Conclusions*

- All parts passed 500 and 1000 hrs NSS
- "White rust" corrosion products are formed from the zinc nickel coating itself
- There was no advantage in using high phosphorus instead of mid phosphorus as an undercoat
  - This is consistent with what is seen using cadmium and other sacrificial coatings

# *20 um High Phos / 10 um Eclipse Black EN*

96 hrs NSS

500 hrs NSS

1000 hrs NSS

# 20 um Mid Phos / 10 um Eclipse Black EN

96 hrs NSS

1000 hrs NSS


500 hrs NSS

# *30 um High Phos / 10 um Eclipse Black EN*

96 hrs NSS

500 hrs NSS

1000 hrs NSS

MacDermid

## *Eclipse Black EN NSS Conclusions*

- Mid Phos EN is not a suitable undercoat for the Eclipse Black EN to pass 500 hrs NSS
- High Phos EN systems can pass 1000 hrs NSS
- Thicker High Phos undercoat gives improved corrosion resistance

# Test Summary NSS

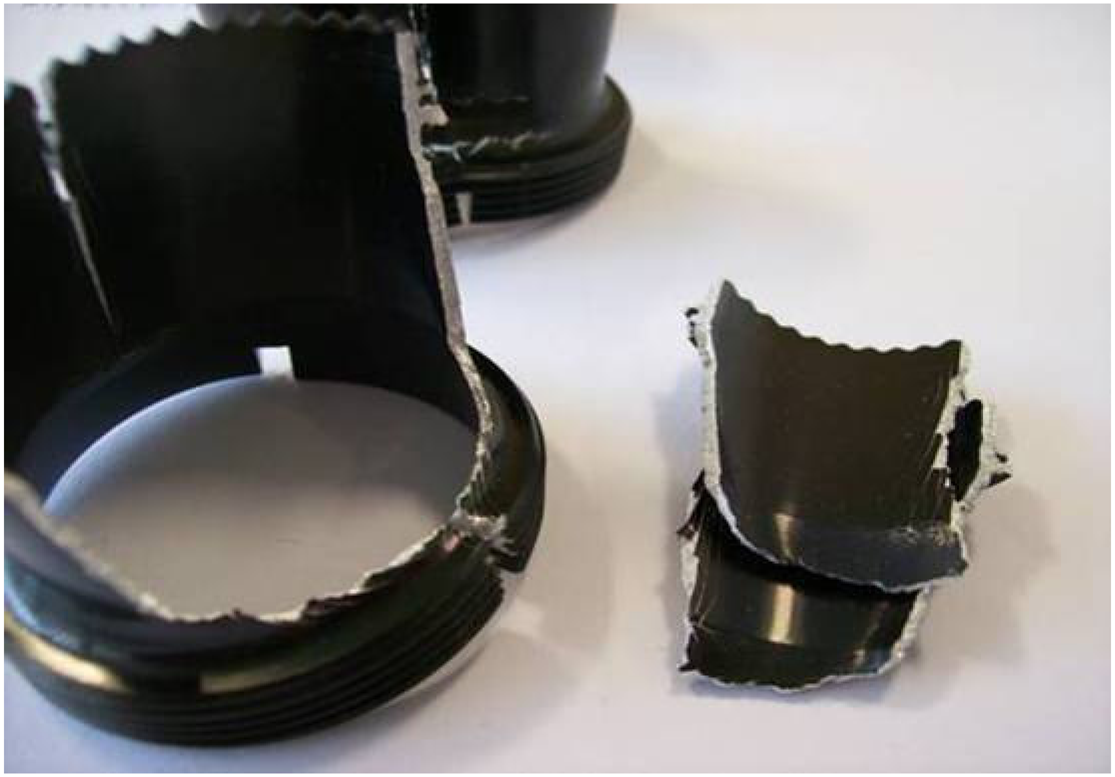
| Base Layer | Top Layer | Result 500 hrs NSS |
|---|---|---|
| High Phos 20 um | EN PTFE 5 um | Passed |
| Mid Phos 20 um | Zinc Nickel 8 um (hexavalent passivate) | Passed |
| High Phos 20 um | Zinc Nickel 8 um (hexavalent passivate) | Passed |
| Mid Phos 20 um | Black EN 10 um (Electro-passivated) | Fail |
| High Phos 20 um | Black EN 10 um (Electro-passivated) | Passed |
| High Phos 30 um | Black EN 10 um (Electro-passivated) | Passed |

MacDermid

# *Connector Adhesion Crush Tests*

# *High Phos / EN PTFE Adhesion*

# High Phos / Zinc Nickel Adhesion



# High Phos / Black EN Adhesion

# *Test Summary Adhesion*

| Base Layer | Top Layer | Adhesion* |
|---|---|---|
| High Phos 20 um | EN PTFE 5 um | Pass |
| High Phos 20 um | Zinc Nickel 8 um (hexavalent passivate) | Pass |
| Mid Phos 20 um | Zinc Nickel 8 um (hexavalent passivate) | Pass |
| High Phos 20 um | Black EN 10 um (Electro-passivated) | Pass |
| High Phos 30 um | Black EN 10 um (Electro-passivated) | Pass |

* "Pass" indicates no blistering, peeling, flaking or separation of plating

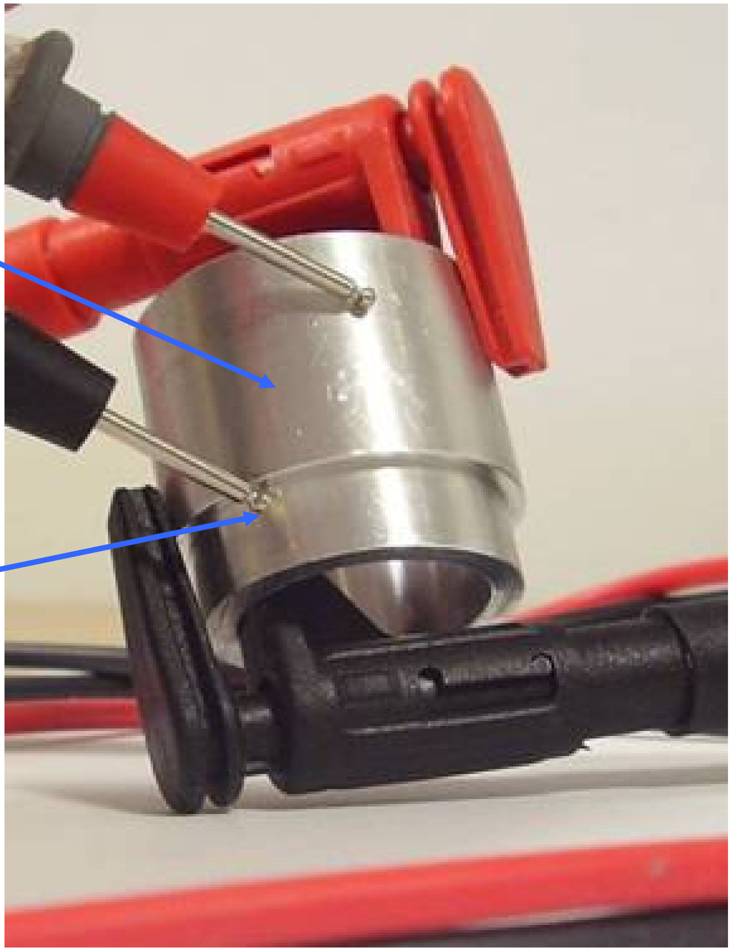
## *Conductivity Test Method*

- Tests carried out on individual shells
- Conductivity measured across 25 mm distance on the shells ($\approx$1 inch)
- Probes have round contact points
- Tested EN/PTFE at various levels of incorporated PTFE

## *Conductivity Testing*

25 mm gap between probes

Probes have rounded ends



MacDermid

# *Conductivity Testing of EN / PTFE*

| PTFE (% by Volume) | Conductivity as plated (mV) | Conductivity after 500 hrs NSS (mV) |
|---|---|---|
| 4% | 2.12 | 1.73 |
| 9% | 1.61 | 1.72 |
| 16% | 1.70 | 1.65 |
| 21% | 2.38 | 1.91 |
| 25% | 2.09 | 1.92 |
| 30% | 2.37 | 2.39 |

## *EN / PTFE Conductivity Conclusions*

- Increased PTFE does not have a significant negative effect on the conductivity, especially after NSS
- Increased PTFE improves the NSS performance
- Incorporation of PTFE into EN deposit changes both conductivity as well as galvanic potential

# *Test Summary Conductivity*

| Base Layer | Top Layer | Conductivity before NSS | Conductivity after 500 hrs NSS |
|---|---|---|---|
| Bare Al shell | | Pass | NA |
| High Phos 20 um | EN PTFE 5 um | Pass | Pass |
| High Phos 20 um | Zinc Nickel 8 um (hexavalent passivate) | Fail[1] | Fail[2] |
| Mid Phos 20 um | Zinc Nickel 8 um (hexavalent passivate) | Fail[1] | Fail[2] |
| High Phos 20 um | Black EN 10 um (Electro-passivated) | Pass | Pass |
| High Phos 30 um | Black EN 10 um (Electro-passivated) | Pass | Pass |

1 “Fail” indicates Millivolt drop >2.5

2 “Fail” indicates Millivolt drop >5.0

MacDermid

## *Electrochemical Potentials*

- Samples plated as described
- Allowed to stabilize in 5% NaCl solution overnight
- Potential measured against Ag/AgCl electrode

# *Electrochemical Potential*

| Deposit | Potential |
|---|---|
| Cadmium (passivated) | -0.625V |
| EN/PTFE (30% by vol) | -0.438V |
| Zn/Ni hexavalent passivate | -0.706V |
| Zn/Ni trivalent passivate | -0.600V* |
| Black EN | -0.588V |

***Test specimens were attacked by the salt solution**

## *Plating Construction Test Matrix*

- Previous tests were all on two layer deposits
- Barrier coatings are more susceptible to porosity causing NSS failures
- Intent is to see the impact of the introduction of a third layer as an aid to reduce porosity
- Results compared to previous dual layer specimens

## *High Phos 15 um + Sulfamate Ni 5 um + Eclipse Black EN 10 um*

**After 500 hrs NSS**

# *High Phos 15 um + Sulfamate Ni 5 um + EN PTFE 5 um*

**After 500 hrs NSS**

# *Plating Construction Summary NSS*

| Base Layer | Middle Layer | Top Layer | Result 500 hrs NSS |
|---|---|---|---|
| High Phos 20 um | | EN PTFE | Pass* |
| High Phos 15 um | Sulfamate Ni 5 ums | EN PTFE | Pass |
| High Phos 20 um | | Black EN Passivated | Pass* |
| High Phos 15 um | Sulfamate Ni 5 ums | Black EN Passivated | Pass |

* From previous tests

# *Plating Construction Summary Conductivity*

| Base Layer | Middle Layer | Top Layer | Conductivity mV | Conductivity mV after 500 hrs NSS |
|---|---|---|---|---|
| High Phos 20 um | | EN PTFE | 2.37* | 2.39* |
| High Phos 15 um | Sulfamate Ni 5 um | EN PTFE | 1.79 | 1.72 |
| High Phos 20 um | | Black EN Passivated | 2.25* | 4.90* |
| High Phos 15 um | Sulfamate Ni 5 um | Black EN Passivated | 2.11 | 3.34 |

* From previous tests

# *Cadmium Alternatives Summary*

## *Review of Coating Options*

- Included Cadmium baseline
- Included Zinc Nickel trivalent passivated
- Included Zinc Nickel hexavalent passivated
- Included EN/PTFE
- Included Black EN
- Omitted Tin Zinc due to poor performance in NSS and conductivity
- Omitted electroplated Aluminum due to negligible market interest
- Omitted ZnCo due to poor performance and negligible market interest

## *Ideal Attributes for a Cadmium Replacement*
### *(From 2010 MacDermid Connector Conference)*

- Conducts current well – resistance below 2.5 milliohms
- Provides good corrosion protection
- Do not produce insulating corrosion products
- Galvanic compatibility with Cadmium
- Durable deposits which withstand mate/unmating
- Non-reflective finish
- Robust, reliable electroplating solutions
- Easily passivated in various colors
- Solderable and able to accept identification markings
- Specification approval
- RoHS compliant

# *Cadmium and Alternatives*
## *(Industry Input From 2011 MacDermid Connector Conference)*

| **Ideal Attributes** | Cd | EN/PTFE | ZnNi & Cr6+ | ZnNi & Cr3+ | Black EN |
|---|---|---|---|---|---|
| Conducts current well – resistance below 2.5 mΩ | | | | | |
| Provides good corrosion protection | | | | | |
| Does not produce insulating corrosion products | | | | | |
| Backward galvanic compatibility with Cd | | | | | |
| Durable deposits that withstand damage | | | | | |
| Robust, reliable electroplating solutions | | | | | |
| Specification approval | | | | | |
| Global environmental compliance | | | | | |
| Non-reflective finish | | | | | |
| Easily passivated in various colors | | | | | |
| Solderable | | | | | |

## ***Revised Ideal Attributes for a Cadmium Replacement***
### ***(Industry Input From 2011 MacDermid Connector Conference)***

- Conducts current well – resistance below 2.5 milliohms
- Provides good corrosion protection
- Do not produce insulating corrosion products
- Galvanic compatibility with Cadmium & Aluminum
- Durable deposits which withstand damage
- Non-reflective finish
- Robust, reliable electroplating solutions
- Overall cost comparable to cadmium standard
- No additional weight compared to cadmium standard
- Solderable
- Accepts identification markings
- Accepts adhesives
- Specification approval
- Global environmental compliance

# What Next?

- No drop-in replacement exists for cadmium (not even cadmium!!)
- The available data on cadmium alternatives is confusing and often contradictory
  - Better control over critical variables of the plating operation are needed during testing
    - Pretreatment
    - Plating construction & total thickness
    - Substrate alloy
    - Part design and machining
- Testing indicates that the most suitable current option for most applications is EN/PTFE using thick or multilayer deposits
  - Need long term service data to address concerns about the barrier coating nature of deposit
  - The facts on outgassing during a fire must be studied and quantified
- Zinc Nickel with both hex and RoHS compliant passivates seems prone to inconsistent conductivity
  - Zinc Nickel forms insulating corrosion products
  - Work is proceeding on improving conductivity

## What Next?

- Black EN may be a viable option
  - More testing is required on all aspects of the deposit
- Other zinc alloys have been tested numerous time by numerous people, but to date none have shown any clear advantages
  - Virtually all testing shows performance worse than EN/PTFE and ZnNi
  - Technology is constantly improving, and these processes should be included in any definitive test matrix
- More data on compatibility with legacy systems is required for all systems
  - There is little data on this, and it is also contradictory
- Other options for cadmium alternatives need to be developed and tested

MacDermid
Industrial Solutions

# ***Thank You!***

Any Questions?